PATENT APPLICATION

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Attorney's Docket No. 2003US312

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

M. Dalil RAHMAN

Serial Number: 10/734,022 Group Art Unit: 1752

Filed: December 11, 2003 Examiner: CHU, John S. Y.

For: **PHOTORESIST COMPOSITION FOR DEEP UV AND PROCESS THEREOF**

**DECLARATION OF M. Dalil Rahman**

August 21, 2006

Mail Stop RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, M. Dalil Rahman, declare as follows:

I am currently employed as a Senior Staff Scientist in the Technology Department of the AZ Electronic Materials Inc. USA, Somerville, New Jersey.

I received a Bachelor of Science degree in Chemistry with Honors in 1973 and a Master of Science degree in Organic Chemistry in 1975 from the Dhaka University, Bangladesh. I was a Research Associate in the Department of Chemistry, at Bangladesh University of Engineering and Technology and a Junior Chemist at AFCC, a Petrochemical Complex in Bangladesh in 1975. Then I joined the Department of Chemistry, Dhaka University as a Lecturer for four



PAGE 16/22 * RCVD AT 8/21/2006 4:24:58 PM [Eastern Daylight Time] * SVR:USPTO-EFXRF-2/11 * DNIS:2738300 * CSID:908 429 3650 * DURATION (mm-ss):05-30

years (1986-1980). I went to Tokyo Institute of Technology in Japan, on a UNESCO Scholarship and received Post Graduate degree in Chemistry in 1981. I did a Doctor of Philosophy degree in organic chemistry from University of Saskatchewan, Saskatoon, Canada in 1985.

I was a Post Doctoral Fellow in University of Montana, Missoula, in 1986, and from 1997 to 1989 was a Research Staff Member in Princeton University, Princeton, New Jersey. I joined Hoechst Celanese Corporation, at Coventry, Rhoce Island and moved to Somerville New Jersey as a Research Scientist in 1993. The name of the company has been changed several times but in fact I have been continuing as a Senior Staff Scientist in Technology Department of AZ Electronic Materials Inc. USA since 1996 to date.

I am the author or co-author of more than 70 publications in chemistry and photolithographic chemistry and have been named as an inventor in over 60 United States Patents or Patent applications.

I have reviewed the Office Action from the United States Patent and Trademark Department dated April 20, 2006, in which all of the claims of the application were rejected as being unpatentable under 35 USC 103(a) as being unpatentable over Nishiyama (US 2004/0063827) in view of Lee et al (US7,022,458).

The following experimental work was undertaken under my supervision.

Example 1: Synthesis of polymer of the present application: Poly(2-methyl-2-adamantyl acetyl norbornene carboxylate(norbornene MAdoc ME) -co-β-methacryloyloxy-γ-butyolactone -co-2-methyladamantyl methacrylate-co-methacryloyloxy-norbornane-butyrolactone-co-maleic anhydride)



PAGE 17/22 * RCVD AT 8/21/2006 4:24:58 PM [Eastern Daylight Time] * SVR:USPTO-EFXRF-2/11 * DNIS:2738300 * CSID:908 429 3650 * DURATION (mm-ss):05-30

A hybrid copolymer was synthesized by reacting 8.16 g of norbornene MAdoc ME( 10 mole%) from Example 1 , 24.15 g of β-methacryloyloxy-γ-butyolactone (GBLMA, 30 mole%), 22.19g of 2-methyladamantyl methacrylate (MAdMA, 40 mole%), 5.26 g of methacryloyloxy-norbornane-butyrolactone (MNBL, 10 mole%) and 2.32 g of maleic anhydride (MA) in the presence of 5 weight% of 2,2'azobisisobutyronitrile (AIBN) in tetrahydrofuran (THF) at 50% solid. The reaction was carried out for 7 hours and the polymer was isolated from diethyl ether twice (1/10 v/v ratio), giving a yield of 33.4g (66.7%). The weight average molecular weight (Mw) as measured on a Gel Permeation Chromatograph (GPC) using polystyrene standards and THF solvent was 16,110.

Photoresist Formulation was made as below:

2.4646 g of polymer from Eexample 1; 0.0416g (30 μmol/g) of triphenylsulfonium nonafluorobutane sulfonate, 0.0416 g (30μmol/g) of 4-methoxy-3,5-dimethyl phenyl dimethyl sulphonium nonaflate, 0.7149 g of 1 weight% propylenegycol monomethylether acetate (PGMEA) solution of N-(1-adamantyl acetamide) and 0.0371 g of 10 weight% PGMEA solution of a surfactant (fluoroaliphatic polymeric ester, supplied by 3M Corporation, St. Paul Minnesota) were dissolved in 26.1588 g of PGMEA, and 0.5502g of gamma valerolactone to give a 30g photoresist solution.

Separately, a silicon substrate coated with a bottom antireflective coating (B.A.R.C.) was prepared by spin coating the bottom anti-reflective coating solution (AZ® EXP ArF-1 B.A.R.C. available from Clariant Corporation, Somerville, NJ) onto the silicon substrate and baking at 175°C for 60 sec. The B.A.R.C film thickness was 37 nm. The photoresist solution was then coated on the B.A.R.C coated silicon substrate. The spin speed was adjusted such that the



PAGE 18/22 * RCVD AT 8/21/2006 4:24:58 PM [Eastern Daylight Time] * SVR:USPTO-EFXRF-2/11 * DNIS:2738300 * CSID:908 429 3650 * DURATION (mm-ss):05-30

photoresist film thickness was 240 nm. The photoresist film was baked at 115°C for 90 sec. The substrate was then exposed in a 193 nm ISI ministepper (numerical aperture of 0.6 and coherence of 0.3/0.7, Annular Illumination). After exposure, the wafer was post-exposure baked at 130°C for 90 sec. The imaged photoresist was then developed using a 2.38 weight% aqueous solution of tetramethyl ammonium hydroxide for 30 sec. The line and space patterns were then observed on a scanning electron microscope. The results are shown in the Table below.

Example 2: Synthesis of equivalent polymer from Lee et al: Poly(5-[2 trifluoromethyl-1,1,1-trifluoro-2-hydroxypropyl]-2-norbornene-co-β-methacryloyloxy-γ-butyrolactone -co-2-methyladamantyl methacrylate-co-methacryloyloxy-norbornane-butyrolactone-co-maleic anhydride)

A hybrid copolymer was synthesized by reacting 15.17 g of 5-[2 trifluoromethyl-1,1,1-trifluoro-2-hydroxypropyl]-2-norbornene ( 10 mole%) , 48.96 g of β-methacryloyloxy-γ-butyrolactone (GBLMA, 30 mole%), 44.99 g of 2-methyladamantyl methacrylate (MAdMA, 40 mole%), 10.66 g of methacryloyloxy-norbornane-butyrolactone (MNBL, 10 mole%) and 4.70 g of maleic anhydride (MA) in the presence of 5 weight% of 2,2'azobisisobutyronitrile (AIBN) in tetrahydrofuran (THF) at 50% solid. The reaction was carried out for 7 hours and the polymer was isolated from diethyl ether twice (1/10 v/v ratio), giving a yield of 70.58g (70.6%). The weight average molecular weight (Mw) as measured on a Gel Permeation Chromatograph (GPC) using polystyrene standards and THF solvent was 15,181.



PAGE 19/22 * RCVD AT 8/21/2006 4:24:58 PM [Eastern Daylight Time] * SVR:USPTO-EFXRF-2/11 * DNIS:2738300 * CSID:908 429 3650 * DURATION (mm-ss):05-30

Photoresist Formulation was made as below:

2.46 g of Poly(5-[2 trifluoromethyl-1,1,1-trifluoro-2-hydroxypropyl]-2-norbornene-co-β-methacryloyloxy-γ-butyrolactone -co-2-methyladamantyl methacrylate-co-methacryloyloxy-norbornane-butyrolactone-co-maleic anhydride)

0.0416g (30 μmol/g) of triphenylsulfonium nonafluorobutane sulfonate, 0.0416 g (30μmol/g) of 4-methoxy-3,5-dimethyl phenyl dimethyl sulphonium nonaflate, 0.7149 g of 1 weight% PGMEA solution of N-(1-adamantyl acetamide) and 0.0371 g of 10 weight% PGMEA solution of a surfactant (fluoroaliphatic polymeric ester, supplied by 3M Corporation, St. Paul Minnesota) were dissolved in 26.1588 g of PGMEA, and 0.5502g of gamma valerolactone to give a 30g photoresist solution.

Separately, a silicon substrate coated with a bottom antireflective coating (B.A.R.C.) was prepared by spin coating the bottom anti-reflective coating solution (AZ® EXP ArF-1 B.A.R.C. available from Clariant Corporation, Somerville, NJ) onto the silicon substrate and baking at 175°C for 60 sec. The B.A.R.C film thickness was 37 nm. The photoresist solution was then coated on the B.A.R.C coated silicon substrate. The spin speed was adjusted such that the photoresist film thickness was 240 nm. The photoresist film was baked at 115°C for 90 sec. The substrate was then exposed in a 193 nm ISI ministepper (numerical aperture of 0.6 and coherence of 0.3/0.7, Annular Illumination). After exposure, the wafer was post-exposure baked at 130°C for 90 sec. The imaged photoresist was then developed using a 2.38 weight% aqueous solution of tetramethyl ammonium hydroxide for 30 sec. The line and space patterns were then observed on a scanning electron microscope. The results are shown in Table below.



PAGE 20/22 * RCVD AT 8/21/2006 4:24:58 PM [Eastern Daylight Time] * SVR:USPTO-EFXRF-2/11 * DNIS:2738300 * CSID:908 429 3650 * DURATION (mm-ss):05-30

Comparative Evaluation:

Table 1 shows the results of the comparative evaluation.

Table 1

| Property of Photoresist | Photoresist containing Polymer(Example 1) of the present invention | Photoresist containing Polymer (Example 2) of the prior art |
|---|---|---|
| Resolution | 90nm (L/S 1:5) | 110nm (L/S 1:5) |
| Depth of Focus | 0.40 μm | Very poor (not measurable) |
| Image Quality | No footing, no scum | Footing and heavy scum |
| Profile | good | Very bad-irregular |
| Photospeed | 19 mJ/cm$^2$ | 18 mJ/cm$^2$ |
| Iso/Dense –Bias(1) | small | Very large |
| Long term stability | 6 months-stable | Less than a month(2) |
| | | |

(1) Bias between imaging isolated lines and densely populated lines on the same wafer, where a small bias is better than a very large bias.

(2) The photoresist containing the polymer of the prior art was evaluated as described above and the photospeed was measured and found to be 18 mJ/cm$^2$. After one month the photoresist was evaluated again to see the change, and in this case the photospeed had changed and found to be less than 5 mJ/cm$^2$ and no image was formed. The photoresist made from the prior art polymer had stability of less than 1 month.

The results show that the photoresist containing the polymer of the present invention provides superior lithographic properties when compared to a photoresist comprising the polymer of the prior art of Lee et al.

I hereby declare that all statements made therein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that



PAGE 21/22 * RCVD AT 8/21/2006 4:24:58 PM [Eastern Daylight Time] * SVR:USPTO-EFXRF-2/11 * DNIS:2738300 * CSID:908 429 3650 * DURATION (mm-ss):05-30

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willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

8-21-06
Date

M Dalil Rahman
Type name of person signing

M. Dalil Rahman
Signature



PAGE 22/22 * RCVD AT 8/21/2006 4:24:58 PM [Eastern Daylight Time] * SVR:USPTO-EFXRF-2/11 * DNIS:2738300 * CSID:908 429 3650 * DURATION (mm-ss):05-30